PREPARATIVE SEPARATION AND CHARACTERIZATION OF COAL LIQUID AROMATICS

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INTRODUCTION

Information concerning the degree and nature of aromaticity in a hydrocarbon feedstock is a very important characterization parameter for refining processes designed to convert high boiling feedstocks into more valuable products. This is especially true in catalytic cracking because feeds of higher aromaticity tend to be more difficult to crack and form coke more easily. Products of the liquifaction of coals are generally highly aromatic in nature and therefore a detailed knowledge of the aromatic structures present in coal liquids is very important in predicting their processing properties.

This work describes the preparative separation and characterization of the aromatics fraction of three Wilsonville coal liquids produced by different two-stage reaction processes. The coals, the liquifaction processes, and the reaction product liquids have been described by Fatemi et. al. (1). The Black Thunder sample was produced by a two stage thermal-catalytic process, while the Illinois No. 6 and Pittsburgh No. 8 liquids were produced using a more severe catalytic-catalytic process.

An additional objective of this work was to characterize the behavior of the DNAP stationary phase in aromatic ring number separations in real samples. Several workers, including this author, have verified the accuracy of the ring number separations on analytical scale DNAP columns using model compounds. However, the limited number of model compounds available, especially of alkyl and naphtheno substituted polynuclear aromatics, and the extremely complex nature of real samples of interest require that such separations be validated more completely using real samples.

EXPERIMENTAL

The samples consisted of the 650-1000 F aromatics fractions of the three Wilsonville coal liquids. One typical petroleum gas oil (650-1000 F) was included for comparison purposes. The aromatics fractions were produced by removal of polar compounds using ion exchange resins, followed by isolation of the aromatics by silica gel chromatography. One milliliter of a 20-30 mg/mL solution of sample dissolved in cyclohexane was injected manually via HPLC sampling valve. The sample was separated by gradient elution using a hexane-MTBE gradient.

The separation on this column is produced via a charge-transfer mechanism in which structures containing larger numbers of aromatic rings (more extensive pi electron systems) are retained by the electron-withdrawing dinitroanaline stationary phase. Use of this phase has been described by Grizzle et. al. (2,3). Data obtained in our laboratory using solutions of model compounds on an analytical scale column showed that the model compounds studied in all cases eluted in the same grouping with others of the same ring number and at increasing retention time with increasing ring number. There was no case in which a compound eluted in the "wrong" group. Alkyl substitution was found to generally not affect retention time enough to move the species out of it's ring number group, although small shifts may occur.

The fractions produced were individually characterized by GC-MS and GC. GC-MS was used to identify individual components of the fractions and as an additional validation of the ring number boundary determinations. Single ion plots of ions representing common structures of different aromatic ring number were used to verify ring number regions. The fraction boundaries were also monitored spectroscopically using a Diode Array Spectrophotometer. The coal liquid fractions were collected in such a way as to attempt to obtain "heart-cuts" from each ring number group, and "boundary cuts" at the borders between groups. Solvents were removed from the fractions by evaporation using a Rotovap and fraction weights were obtained. Total recoveries of injected sample were 97% to 104%.

RESULTS

Cut points for the ring number fractions were initially estimated using model compounds. Model compounds known to lie on the boundaries of ring number regions were injected to define initial cut points between regions. These initial cut points were determined to be approximately 19.5 minutes for the 1-2 ring separation, 40 min for 2-3 ring, 60 min for 3-4 ring, and 80 min for 4-5+ ring. A 30 minute backflush step was included to completely elute the sample. Since total column capacity was limited to 20-25 milligrams to avoid overloading, and about twenty fractions were taken, fraction sizes were limited to a few milligrams at most in each fraction.

The samples used for this work were in the boiling range of petroleum gas oils, 650-1000 F. The molecular weight range was typically 200-600 Daltons with an average of about 350, as measured by mass spectroscopy. This means that for a molecule to contain only one aromatic ring, typically 70-80 percent of the atoms must be present in nonaromatic portions of the molecule. In general, increasing nonaromatic content results in increasing fraction complexity. Increasing aromaticity restricts the number of possible compound structures within a particular molecular weight range by constraining the hydrocarbons to a limited number of structures, since those structures must contain aromatic rings. Hence one of the effects were observe is that the ring number fractions become less complex as we go to higher ring numbers as a result of the decreasing variety of alkyl and naphthene substitution.

For comparison and validation purposes mass spectral data were collected by low resolution, high voltage MS using the so-called "Robinson" method (4). Table I shows a comparison of the normalized ring number distributions obtained by preparative HPLC, compared to those obtained from hydrocarbon type analysis by mass spectroscopy. Good agreement is obtained generally within the limits of the techniques used.

The liquid chromatographic separations showed the bulk of the mass isolated from the Illinois No. 6 and the Pittsburgh No. 8 liquid to consist of one and two ring material, which is consistent with the MS results. Chromatograms for these samples are very similar. These two samples represent the coals produced from a two stage, catalytic-catalytic process described in Reference (1). The fractions isolated from the Black Thunder (Wyodak) coal liquid, which were produced by a Thermal-Catalytic process, showed a much larger fraction of 3 and 4 ring material, compared to the Pittsburgh and Illinois coal liquids. The amount of one and two ring material is relatively small. Petroleum gas oil fractions showed a wide distribution of ring number structures with 1- and 2- ring structures predominating.

CHARACTERIZATION OF FRACTIONS

UV Spectra

All HPLC separations were monitored spectrophotometrically by continuous collection of spectra in the ultraviolet region. Aromatic compounds show characteristic spectra which differ significantly depending on ring number. This is a result of the extension of the aromatic ring system, which increases the probability of lower energy, longer wavelength transitions. Shifts to absorption at longer wavelengths will occur as the aromatic structures are extended to larger ring numbers. UV absorption spectra were used to help define the boundaries of the separation. Spectra from the separation of the Pittsburgh coal liquid are shown in Figure 1 to illustrate the distinct spectral changes which occur in the ring number separation. Figure 1a shows how the spectra change in the 1-2 ring transition region of the Pittsburgh coal liquid separation. All spectra are normalized to the absorbance maximum. It is clear that a distinct change occurs in the spectra of eluted sample components as we go from spectrum C in Figure 1a, taken at 19 minutes, to D, taken at 20 minutes. Spectrum C is much more typical of a one ring aromatic while spectrum D more closely resembles a two ring aromatic compound. These spectral changes are consistent with model compound data which shows the 1-2 ring transition to occur at about 19.5 minutes.

Figure 1b shows the sharp spectral transition occurring over just two minutes in the portion of the separation where 3 ring compounds begin to emerge. The much more extended absorption of spectrum B is indicative of the partial transition to 3 ring structures.

Figure 1c shows evidence of the emergence of 4 ring structures. Spectrum A is a typical 3 ring region spectrum, while spectrum B shows the emergence of

a series of bands in the region from 300 to 340 nm which is typically characteristic of 4 ring aromatics.

Figure 1d shows more clearly the difference between characteristic spectra taken from the middle region of each ring type.

Gas Chromatography and GC-MS

All of the fractions from the Pittsburgh No. 8 separation, and selected fractions from the other separations, were analyzed by high resolution capillary gas chromatography. Peak identification was performed by gas chromatography-mass spectroscopy and retention time matching with standard solutions of polynuclear aromatic mixtures. The variety of structures can be qualitatively compared by means of the number of distinct peaks observable in the chromatograms. All of the 1 ring fractions appeared to possess a large variety of structures and individual components are not well resolved into distinct peaks. Chromatographic resolution is also not complete enough to be able to identify individual components unambiguously by GC-MS. However, GC-MS data obtained from these fractions is consistent with the predominance of heavily alkyl substituted one ring aromatic structures. The two ring region was found to contain primarily alkyl diaromatics, including hexahydropyrenes, naphtheno and dinaphthenonaphthalenes, as well as alkyl acenaphthenes, but there was no evidence of 3 ring aromatics. The 2-3 ring boundary fraction contained hexahydropyrene, alkyldihydroanthracenes, and alkyl phenanthrenes. The 3 ring region showed alkylated anthracenes, phenanthrenes, and naphthenophenanthrenes as as well as alkyl benzofluorenes. The chromatograms from the four ring region showed exclusively alkylated tetraaromatics, including pyrenes, benzophenanthrenes, and benzanthracenes. A number of components, including pyrene and methyl pyrenes appear in several of the later fractions, providing evidence of significant bandspreading in this part of the liquid chromatographic separation. All gas chromatograms from this region show relatively few compounds and demonstrate a tremendous reduction in complexity which can be achieved by using LC and GC together to characterize complex hydrocarbon mixtures. Even the petroleum gas oil is vastly reduced in complexity. The backflush fraction of the Pittsburgh coal liquid shows the presence of 4, 5, and 6 ring aromatics. Model compound data from HPLC separations on DNAP indicate that ring number separations are increasingly poorly resolved above 5-6 rings, and this appears to be borne out by the wider variety of multi-ring structures appearing in this fraction.

GC-MS Verification of HPLC Ring Number Regions

GC-MS data obtained from the individual fractions were used in an additional way to verify ring number region assignments. Constraints imposed by structural and molecular weight requirements mean that some fragment masses will be much more likely to appear in the mass spectra of aromatics and substituted aromatics than others. The problem is greatly simplified by the absence of large amounts of nitrogen, oxygen, and sulfur containing compounds. Low sulfur content allows us to eliminate consideration of sulfur containing structures for the coal liquids, but not the petroleum gas oil, which contains 2.8 per cent sulfur. A consideration of the likely representative structural combinations and ions produced from those structures shows that by monitoring for a limited set of single ions representing likely fragments or molecular ions from those structures, we can characterize the ring number distribution for the sample by determining whether the observed masses are consistent with the expected ring number. For example, masses 270 and 280 are likely masses from 1 ring aromatics possessing typical alkyl or naphthenic substitution. The region of mass 270-280 was chosen because it is the minimum mass range of 6 ring aromatics. Since the average MW of these compounds is about 350, ions in this mass range will almost always represent the larger of any fragment ions produced. Unsubstituted, or minimally substituted 3 ring or 4 ring compounds such as pyrene and methyl pyrenes will not be observed within this mass range, but their elution positions in the HPLC separation are already well known from model compound studies. Masses 280 and 276 are likely products of 2 ring aromatics, and mass 276 of 3 ring aromatics. Likely masses for 4, 5 and 6 ring aromatics are derived from the same set, 270 and 276 for 4 rings, 280 for 5 rings, and 276 for 6 rings. Thus by monitoring for only three ions, 270, 280, and 276, and by reasoning that 4 ring aromatics will not likely fall into the same LC ring fraction as 1 or 2 ring aromatics, and 5 ring aromatics will not coelute with 2 ring, etc. we can obtain additional confirmation of the ring number content of each fraction by GC-MS. Of course this procedure may not work for some unusual structure types, some of which

we must expect, but it should hold true for most common structures such as those found in these fractions.

Figure 2 shows the GC-MS single ion chromatograms for 1 through 4 ring fractions of the Illinois coal liquid. Figure 2a shows the predominance of masses 270 and 280 in the 1-ring fraction. The absence of mass 276 suggests the absence of significant 2 or 3 ring material in this fraction. A heart cut of the 2 ring region taken from the Illinois coal liquid is shown in Figure 1b. No significant signal at mass 270 is found in this Figure indicating that no 1 ring material overlapped the fraction. Figure 2c shows exclusively 3 ring material in the 3 ring fraction as evidenced by the presence in significant quantity of only mass 276. Figure 2d shows a fraction from the 4 ring region containing exclusively ion mass 270, suggesting a relatively pure 4 ring fraction, without significant 3 or 5 ring "contamination". Similar ion chromatograms from later fractions showed significant overlap between 5 and 6 ring components.

CONCLUSIONS

The preparative DNAP column was found to effectively separate coal liquid aromatics fractions by ring number with only limited overlap. Distinct changes in UV spectra and GC-MS data were observed in the same boundary regions between ring numbers determined by use of model compounds. Boundary regions were less sharp for the petroleum gas oil as a result of the greater degree of alkyl substitution and the presence of significant sulfur containing components. Preparative HPLC is seen to be a very effective way of simplifying complex hydrocarbon mixtures for further study and characterization. The coal aromatics were found to consist mainly of polynuclear aromatics with limited alkyl substitution. This was especially true of the Black Thunder Coal liquid, which contained primarily 3, 4 and 5 ring material. The larger ring structures in the Black Thunder material were probably the result of the thermal-catalytic two-stage liquification process used in it's preparation. The Pittsburgh and Illinois coals were produced using a more severe catalytic-catalytic process and, as a result, contained generally smaller aromatic ring structures. The petroleum gas oil was found to contain more heavily alkyl substituted structures than the coal liquids, based on differences in UV spectra and gas chromatogram complexity. Gravimetric quantification of coal liquid ring fractions yielded results for ring number distributions similar to those obtained by low resolution, hydrocarbon type mass spectroscopy.

REFERENCES

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TABLE I

RING NUMBER DISTRIBUTION BY PREPARATIVE HPLC COMPARED TO MASS SPECTROSCOPY

	Aromatic Rings				
	1	2	3	4	5+
Illinois No. 6					
HPLC	22.7%	48.2%	20.2%	8.5%	0.4%
MS	23.3	37.3	21.7	11.4	0.4
Black Thunder					
HPLC	12.1	24.8	19.3	37.1	6.7
MS	14.4	23.0	23.9	29.5	2.1
Pittsburgh No. 8					
HPLC	30.2	36.9	18.9	11.9	1.7
MS	29.7	33.2	18.4	13.7	1.1

Notes:
1. All HPLC data were obtained using the same dividing points. Dividing points were identified by spectra, model compounds, and GC-MS.
2. MS data do not add up to 100% because of the presence of unidentified species in the MS results.

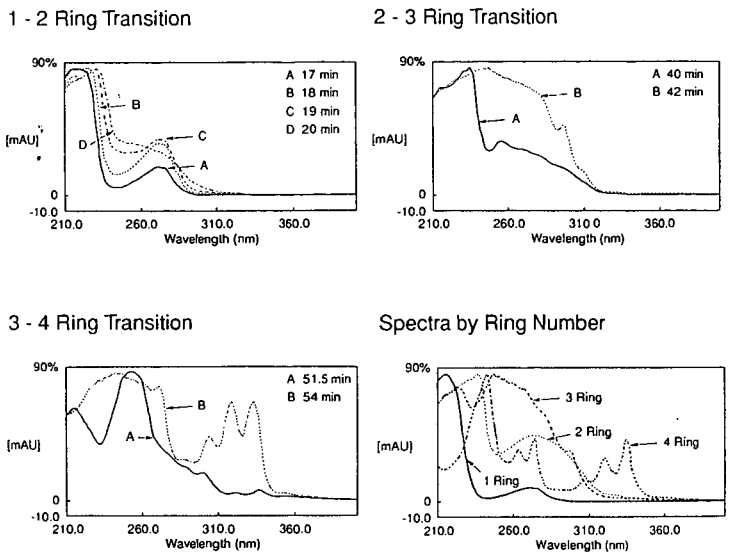

Figure 1. UV Spectra at different retention times.

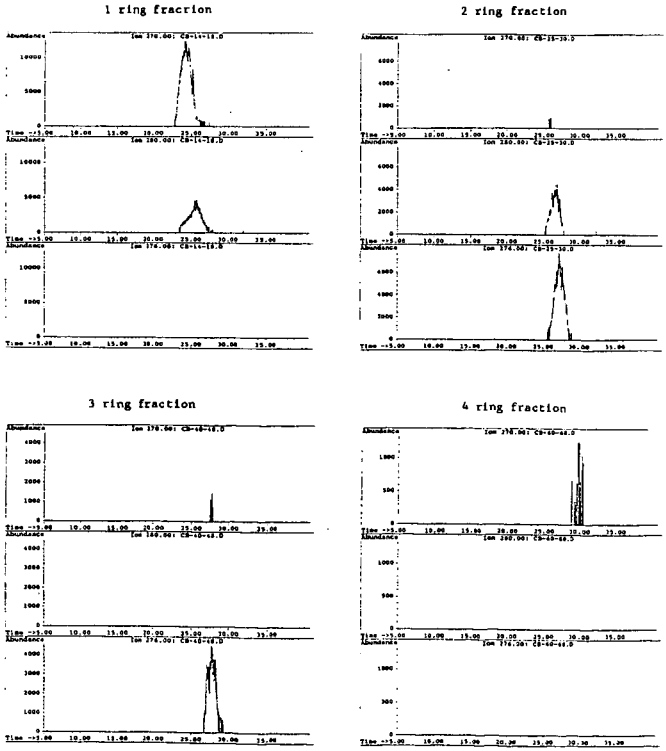

Figure 2. GC-MS ion chromatograms of ring fractions of Illinois No. 6 coal liquid.